REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
05-31-2011

2. REPORT TYPE
Final Report

3. DATES COVERED *(From - To)*
03-1-2010 - 02-28-2011

4. TITLE AND SUBTITLE
A New Scheme for the Detection of Optical Radiation in the External Photoemissive Mode: Device Implementation

5a. CONTRACT NUMBER
FA9550-10-1-0049

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Howard University 2300 6th Street NW, Room 1016

8. PERFORMING ORGANIZATION REPORT NUMBER
53-0204707

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR 875 N. Randolph Street, Suite 324, Room 3112, Arlington VA 22203-1768

10. SPONSOR/MONITOR'S ACRONYM(S)
AFOSR

11. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFRL-OSR-VA-TR-2012-0774

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The work undertaken this year included setting up equipment for and making absorption measurements of Ag/n-Si composite films containing 3x10e+19 per cubic centimeter of antimony and various Ag at. %. The absorption was greater than 50 % from 1-14 microns wavelength. A complete inhouse responsivity facility was setup for measuring responsivity, signal-to-noise ratios and detectivity for composite films from room down to liquid nitrogen temperatures. Those films containing 13 at. % Ag were found to have the highest responsivity. Room temperature responsivities in the 1-2 micron wavelength were routinely fabricated and found to be due to composite behavior and not due to the silicon matrix alone. Transport measurements indicated that in films with greater than 20 at. % Ag, the Ag acted as a dopant producing room temperature carrier concentrations larger than three orders of magnitude than that due to the antimony alone, producing films with extremely low resiistivities and very narrow depletion regions between the Ag and Si. This will help to make tunneling of photoexcited electrons from the Ag nanoparticles into the silicon conduction band much easier.

15. SUBJECT TERMS

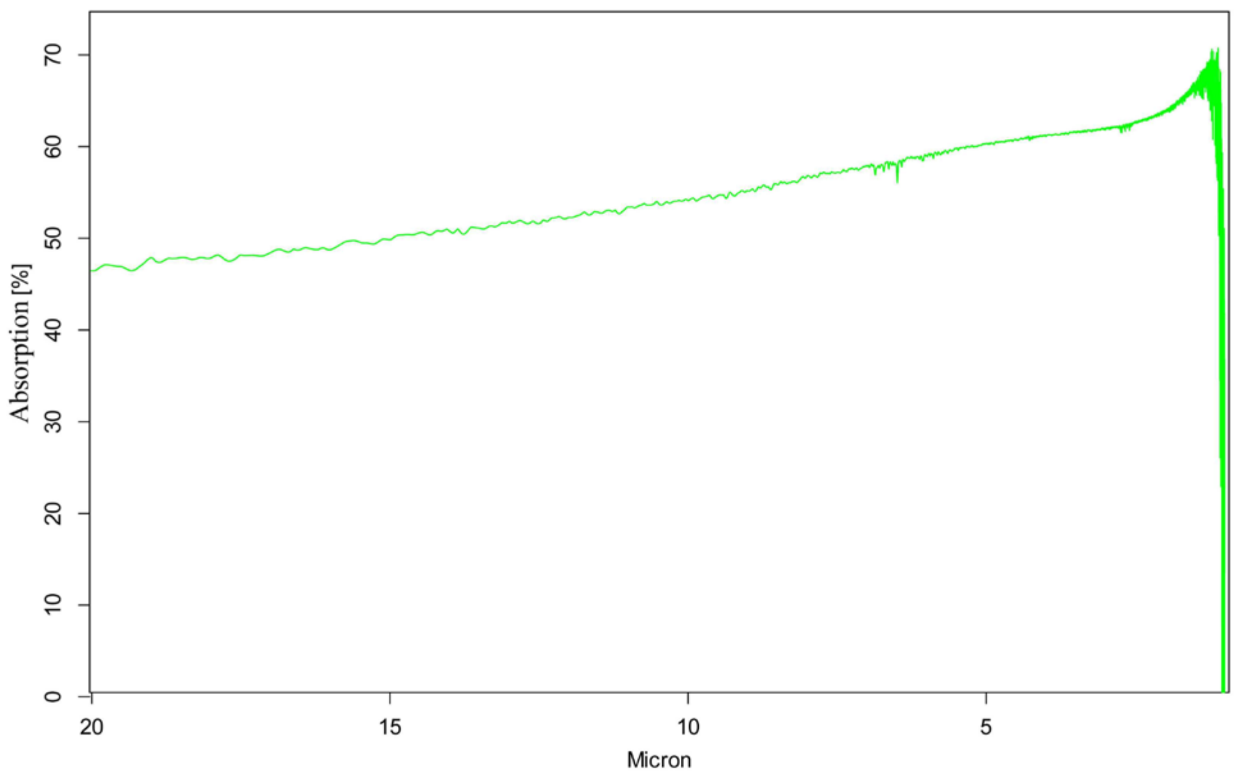
16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
U	U	U	UU		Caribbean Ross

19b. TELEPONE NUMBER (*Include area code*)
202-238-2580

A New Scheme for the Detection of Optical Radiation in the External Photoemissive Mode: Device Implementation. FA9550-10-0049

Final Technical Report

1. Optical Absorption Measurements



In the Figure above we show the optical absorption of a Ag/n-Si composite film containing 20 at. % Ag that was 5μm thick and prepared at 550 C on a high resistivity Si(111) substrate. This absorption is typical of composite films prepared with 13-20at. % Ag. The measurement was made using a Bruker FTIR Spectrophotometer. It is to be noted that the absorption is > 50 % from 1-14μm dropping to about 47% at 20μm wavelength. A high absorption is desired for good detection and this is quite a noteworthy result for this system.

II. Radiometric Measurements

In our Ag-Si composite film studies we used mainly n-type doped silicon, though we did prepare some Ag-Si films with p-type silicon targets. In particular we found that a 5μm thick film prepared at 550 C by magnetron co-sputtering from Ag and p-type Si (boron doped) targets containing 13 at. % Ag in a p-type Si matrix with a resistivity between 1-2Ω-cm produced a signal current at room temperature when irradiated with a blackbody source at 900 C through a 1-1.5μm band-pass filter. The Ag nanoparticles had an average size of 15nm. With a 5μm thick p-type Si film without Ag, no signal current was observed. Thus the current was due to the presence of the Ag nanoparticles.

This presents itself as an opportunity to use such Ag in p-type Si films in n-p junction polycrystalline Si solar cells to increase the photo-generated current in the p-type absorbing layer. There are two things to be noted here. First the response to the solar spectrum is extended to 1.5µm that is beyond the 1.1µm due to silicon. This is a small but significant improvement as the solar spectrum becomes quite small beyond this point. Secondly the plasmon resonances for Ag nanoparticles in Si appear at wavelengths larger than 370 nm giving responses in the visible part of the electromagnetic spectrum depending on the composite film microstructure. As these plasmons can be damped by photoexcitation of bound electrons into the conduction band another source of signal current becomes possible. And because these plasmon absorptions are much larger than that due to silicon, thinner film structures leading to cheaper solar cells may be realized. The objectives of the research is to determine and construct Ag-Si composite films with the optimum microstructure of Ag nanoparticles (size, distribution and volume fraction) embedded in a p-type silicon matrix with a determined thickness with a resistivity in the 1-5Ω-cm range for use as the p-type absorbing layer in a n-p junction polycrystalline silicon solar cell. The quantum efficiencies of these composite solar cells will be compared to those not containing Ag nanoparticles.

III. Hall Measurements and N-Type Doping of Silicon using Ag Nanoparticles

The resistivity of heavily doped polycrystalline silicon films are limited by the amount of dopant that can be incorporated in substitutional sites in the grains. High n-type doping concentrations of $10^{19}/cm^3$ produce typical room temperature resistivities of $5x10^{-2}$ Ω-cm in polycrystalline silicon films with an average grain size of 100 nm. It is demonstrated in this study that room temperature resistivities of $3x10^{-2}$ Ω-cm with the same doping concentration as given above may be obtained with an average grain size of 16 nm if at least 20 at. % Ag is incorporated in these films. This comparable resistivity with a smaller grain size (which should give rise to larger resistivities) and the same n-type doping indicates that the Ag acts as a dopant in these films as the room temperature carrier concentrations are three orders of magnitude larger than the n-type dopant concentration.

1. Introduction

Heavily doped polycrystalline silicon films are widely used as gate electrodes, emitters and diffusion sources for shallow junctions. These highly doped films are characterized by a low resistivity, but are limited by the amount of the dopant that can be incorporated in substitutional sites in the grains. The resistivities are also limited by the grain sizes, with films having smaller grains giving rise to more grain boundaries and larger resistivities. Grain size is a function of film preparation and can vary over a wide range, typically from tens of nanometers [1] to tenths of microns [2] depending on how the films are fabricated, with resistivities no smaller than 10^{-2} Ω-cm regardless of the doping. Films with 100 nm grain sizes with dopant concentrations of $3x10^{19}/cm^3$ have been fabricated with a room temperature resistivity of $5x10^{-2}$ Ω-cm [1] and will be used to compare with films prepared in this work. The results presented here came from a study of Ag/n-Si composite films that are being investigated for another application that is discussed below.

Heavily doped Ag/n-Si composite films are being studied for use as infrared detectors, in particular for sensing radiation in the earth's atmospheric windows, i.e. 1-2, 3-5 and 8-14µm wavelength ranges [3]. Films presently under investigation contain 13-20 at. % Ag with Ag particle sizes of 16 nm embedded in n-type Si matrices with antimony dopant densities of $3x10^{19}/cm^3$. They are 3-5 microns thick [4]. The Ag content is a compromise between having a sufficient quantity for good signal detection but a small enough amount to avoid generating percolation paths. The thicknesses have been shown to give high absorption (50-70%) over a wavelength range of 1-15µm [5].

The Ag nanoparticles produce buried Schottky barriers in the Si. In order for electrons which are photoexcited in the Ag nanoparticles to reach the Si conduction band to generate a signal, they must either surmount this barrier or tunnel through it, depending on their energies. Since the experimental barrier height has been measured to be between 0.6-0.7eV [6], electrons excited by radiation in the 3-5µm and 8-14µm atmospheric windows must tunnel through it as their energies are smaller than this height.

Ag was chosen for this application because it has an extremely small solubility in silicon at the highest temperatures (~700^oC) that may be used in preparing composite films. It forms no silicides meaning that no compounds will be formed when making films of various Ag particle sizes, volume fractions and distributions. This composite also provides a non-toxic, simple detector system alternative employing silicon-based technology. Small Ag particles are desired as they give higher photoresponses than larger ones [7]. It was found that depositing films on substrates at a temperature of 550^oC produced a narrow distribution of both Si and Ag equiaxed particles 16 nm in size [4]. Though larger Si crystallites are desired for good transport of photoexcited electrons, the higher deposition temperatures required to achieve this would produce larger and less photosensitive Ag particles.

In a previous publication [3] it was shown that in heavily doped n-type Ag-Si composite films, quantum mechanical tunneling of electrons at room temperature can occur at incident radiation wavelengths of 3, 5, 8 and 14µm when electric fields on the order of 10^6 V/cm are applied across the Ag-Si depletion regions. Quantum efficiencies between 10-35% are possible depending on the wavelength of the incident radiation. The use of n-type Ag-Si composite films with doping densities in the 10^{19}-$10^{20}/cm^3$ range produce small Ag-Si depletion region widths close to 4nm. This combined with applying fields of 10^6 V/cm is the approach that is being pursued in an attempt to produce films with responsivities in the earth's atmospheric windows at room temperature.

It was during measurement of the transport properties of these films, in particular of the effects of the amount of Ag in them, was it found that the Ag particles acted as a dopant in the Si matrix.

2. Theoretical Considerations

Metal nanoparticles embedded in semiconductors can produce a number of interesting effects and properties that are functions of the materials involved [8]. While ErAs particles in GaAs produced a resistive material [9], ErAs particles in InGaAs were found to act as a dopant contributing electrons to the semiconductor [10]. The Schottky barrier created by the interface can pin the Fermi level in the semiconductor and for some materials the Fermi level may lie near the band edge of the semiconductor and for others near the middle of the gap. If located near the middle of the gap, the metal particles can deplete the surrounding carriers and lead to a more resistive material. If the Fermi level is near the band edge, the metal can contribute electrons/holes to the semiconductor, acting as a dopant. We found in this investigation that at 20 at. % Ag and above the Ag acts a dopant in the silicon and below this value the antimony is the only dopant contributing to the carrier density..

3. Experiment

Films used in the transport data presented were 1µm thick. They were produced by magnetron co-sputtering onto high resistivity (>10^3Ω-cm) 3-in. diameter Si (111) substrates, held at 550°C, using a Kurt J. Lesker CMS-18VHV Thin Film Deposition System. The targets were 99.999% pure Ag and 99.999% pure n-type Si with an antimony concentration of $3\text{x}10^{19}$ cm^{-3}. A SIMS analysis of deposited films showed a uniform concentration of antimony from the composite surface to the silicon substrate, independent of film thickness.

In order to determine the effects of Ag concentration on transport properties films with 22, 16 and 13 at. % Ag were used. These percentages were obtained by varying the Ag deposition rate and verified by both Rutherford Backscattering (RBS) and Energy Dispersive Spectroscopy (EDS). The average Ag and Si crystallite size of 16nm was measured using x-ray diffraction reported in a previous publication [11]. Samples used for these measurements were approximately 1 centimeter square. Four ohmic contacts were applied onto the corners of each sample.

Hall measurements were made using a MMR Technologies, Inc. Hall measurement system. This apparatus used the Van der Pauw technique to measure resistivity, carrier density and type. Measurements were taken from 77K up to 500K using a magnetic field of 1 Tesla. All measurements were made with small electric fields (<$3\text{x}10^{-2}$V/cm).

4. Experimental Results

Figure 1 gives a plot of carrier concentration over the temperature range 77 – 500K. In this figure it is to noted that the room temperature carrier concentrations for samples with 13 and 16 at. % Ag are very close in value and equal to $1.5\text{x}10^{19}/cm^3$, close to the dopant density of $3\text{x}10^{19}/cm^3$, while that with 22 at. % Ag is three orders of magnitude larger. These values persist down to liquid nitrogen temperatures. In Figure 2 is plotted the resistivity vs 1/kT for this same temperature range. The room temperature resistivities are 0.03, 0.75 and 1.25 Ω-cm for films with 22, 16 and 13 at. % Ag respectively. Resistivities have been measured for heavily doped n-type polycrystalline silicon with doping concentrations of $3\text{x}10^{19}/cm^3$ and grain sizes comparable to those measured in this work (16 nm) with values close to the films with 16 and 13 at. % Ag [1], but resistivities in the 0.02 – 0.03 Ω-cm range typically occur in heavily doped polycrystalline silicon films with larger grain sizes of 75 nm [12].

It was found in these investigations that films prepared with Ag concentrations of 20 at. % and higher resulted in carrier concentrations at room temperature that were three orders of magnitude higher than the dopant densities, with resistivities in the 0.03 Ω-cm range. Recently, a 5µm thick film with 20.5 at. % Ag was fabricated with a room temperature resistivity of only $3.91\text{x}10^{-3}$ Ω-cm. Since it was prepared under the same conditions as other films in this study ($3\text{x}10^{19}/cm^3$ antimony doping concentration deposited on substrates at 550 C) with a resistivity considerably lower than 0.03 Ω-cm, an investigation will be undertaken to determine if there is a critical Ag concentration near 20 at. % which produces the lowest resistivities under the present deposition conditions.

5. Conclusions

Ag nanoparticles embedded in heavily doped n-type polycrystalline silicon can provide an additional doping concentration if the Ag concentration exceeds a certain amount. In particular it is found that in Ag-Si composite films prepared at 550 C doped with $3x10^{19}/cm^3$ of antimony, the Ag exists as nanoparticles 16 nm in size and increases the free carrier concentration by three orders of magnitude if the film contains at least 20 at. % Ag. Under these conditions the resistivities of these polycrystalline films can be made very small, comparable to those with much larger crystallites and hence are useful in applications such as gate electrodes and diffusion sources for shallow junctions. This work has also indicated that resistivities as low as that of single crystalline silicon with n-type doping concentrations in the $10^{19}/cm^3$ range is possible under deposition temperatures as low as 550 C.

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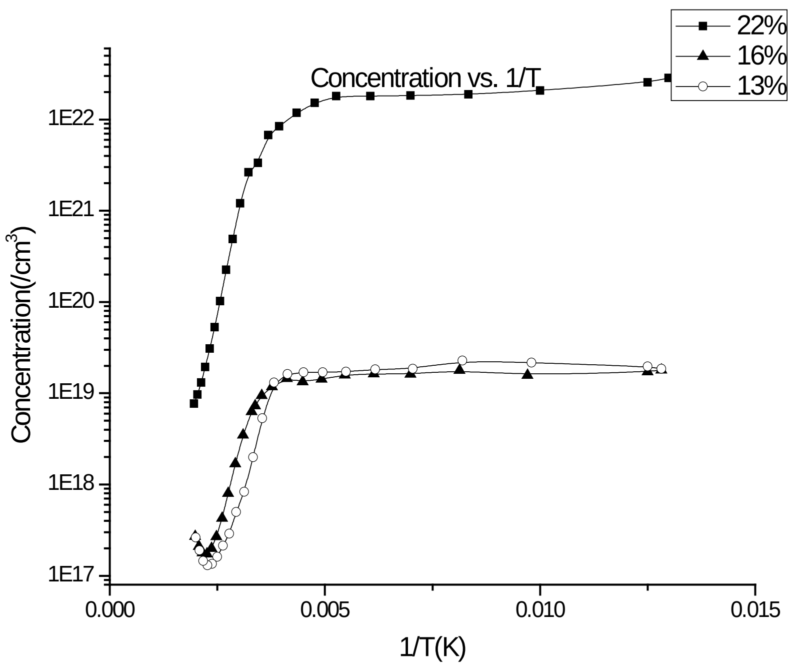
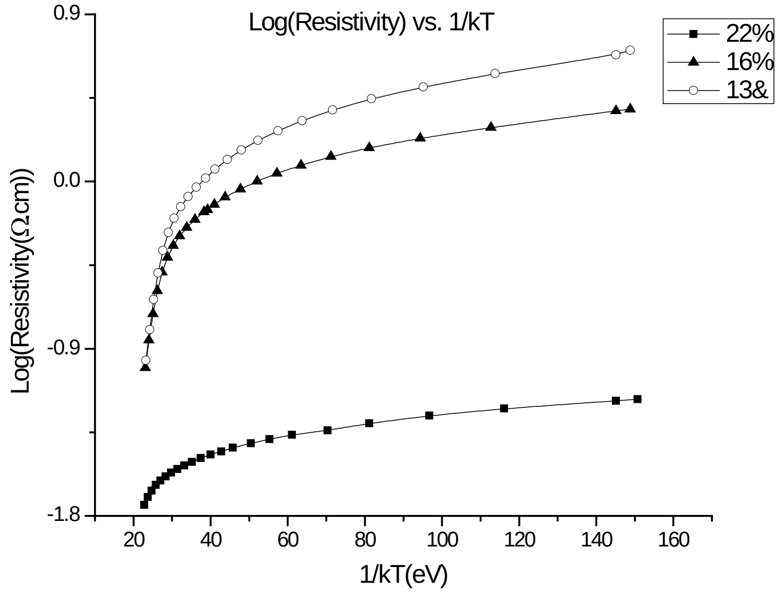
Figures



Concentration vs. 1/T
22%
16%
13%
1E22
1E21
1E20
1E19
1E18
1E17
Concentration(/cm^3)
0.000
0.005
0.010
0.015
1/T(K)



IV. Room Temperature Responsivity in the 1-2µm Wavelength Range

As was demonstrated in an earlier publication (Jour. Appl. Phys. 104, 076101 (2008), room temperature quantum efficiencies of 10-35% are possible at 3, 5, 8 and 14 µm depending on the wavelength of the incident radiation, a study was undertaken to produce room temperature responsivities in the earth's three atmospheric windows at 1-2, 3-5 and 8-14µm wavelengths. It was found possible to produce such a result in the 1-2µm window not due to the silicon matrix in films 5µm thick containing 13 at. % Ag and $10^{19}/cm^3$ n-type doping that was deposited at 550 C and subsequently annealed in Ar gas at 600 C for 30 minutes. It is believed at this time that a post deposition treatment such as annealing or rapid thermal annealing may hold the key to obtaining room temperature responsivities in the 3-5 and 8-14µm windows and present efforts are being directed along these lines.